WEST

End of Result Set

Generate Collection | Print

L7: Entry 1 of 1 File: USPT Jun 9, 1998

DOCUMENT-IDENTIFIER: US 5763548 A
TITLE: (Co)polymers and a novel polymerization process based on atom (or group) transfer radical polymerization

US Patent No. (1):
5763548

claims 5-7.

Detailed Description Text (10):
In the present invention, any radically polymerizable alkene can serve as a monomer for polymerization. However, monomers suitable for polymerization in the present method include those of the formula: ##STR2## wherein R.sup.1 and R.sup.2 are independently selected from the group consisting of H, halogen, CN, CF.sub.3, straight or branched alkyl of from 1 to 20 carbon atoms (preferably from 1 to 6 carbon atoms, more preferably from 1 to 4 carbon atoms), .alpha.,.beta.-unsaturated straight or branched alkenyl or alkynyl of 2 to 10 carbon atoms (preferably from 2 to 6 carbon atoms, more preferably from 2 to 4 carbon atoms), .alpha.,.beta.-unsaturated straight or branched alkenyl of 2 to 6 carbon atoms (preferably vinyl) substituted (preferably at the .alpha.-position, with a halogen (preferably chlorine), C.sub.3 -C.sub.8 cycloalkyl, phenyl which may optionally have from 1 to 5 substituents on the phenyl ring selected from the group consisting of C.sub.1-6 -alkyl, C.sub.1-6 -alkenyl (preferably vinyl), C.sub.1-6 -alkynyl (preferably acetylenyl), C.sub.1-6 -alkoxy, halogen, nitro, carboxy, C.sub.1-6 -alkoxycarbonyl, hydroxy protected with a C.sub.1-6 -acyl, cyano and phenyl, hetercyclyl, C(.dbd.Y)R.sup.5, C(.dbd.Y)NR.sup.6 R.sup.7 and YC(.dbd.Y)R.sup.8, where Y may be NR.sup.8 or O (preferably O), R.sup.5 is alkyl of from 1 to 20 carbon atoms, alkoxy of from 1 to 20 carbon atoms, aryloxy or heterocyclyloxy, R.sup.6 and R.sup.7 are independently H or alkyl of from 1 to 20 carbon atoms, or R.sup.6 and R.sup.7 may be joined together to form an alkylene group of from 2 to 5 carbon atoms, thus forming a 3- to 6-membered ring, and R.sup.8 is H, straight or branched C.sub.1 -C.sub.20 alkyl or aryl; and

Detailed Description Text (15):
Furthermore, in the present application, "aryl" refers to phenyl, naphthyl, phenanthryl, phenalenyl, anthracenyl, triphenylenyl, fluoranthenyl, pyrenyl, pentacenyl, chrysenyl, naphthacenyl, hexaphenyl, picenyl and perylenyl (preferably phenyl and naphthyl), in which each hydrogen atom may be replaced with alkyl of from 1 to 20 carbon atoms (preferably from 1 to 6 carbon atoms and more preferably methyl), alkyl of from 1 to 20 carbon atoms (preferably from 1 to 6 carbon atoms and more preferably methyl) in which each of the hydrogen atoms is independently replaced by a halide (preferably a fluoride or a chloride), alkenyl of from 2 to 20 carbon atoms, alkynyl of from 1 to 20 carbon atoms, alkoxy of from 1 to 6 carbon atoms, alkylthio of from 1 to 6 carbon atoms, C.sub.3 -C.sub.8 cycloalkyl, phenyl, halogen, NH.sub.2, Cl.sub.1 -C.sub.6 -alkylamino, C.sub.1 -C.sub.6 -dialkylamino, and phenyl which may be substituted with from 1 to 5 halogen atoms and/or C.sub.1 -C.sub.4 alkyl groups. (This definition of "aryl" also applies to the aryl groups in "aryloxy" and "aralkyl.") Thus, phenyl may be substituted from 1 to 5 times and naphthyl may be substituted from 1 to 7 times (preferably, any aryl group, if substituted, is substituted from 1 to 3 times) with one of the above substituents. More preferably, "aryl" refers to phenyl, naphthyl, phenyl substituted from 1 to 5 times with fluorine or chlorine, and phenyl substituted from 1 to 3 times with a substituent selected from the group consisting of alkyl of from 1 to 6 carbon atoms,

alkoxy of from 1 to 4 carbon atoms and phenyl. Most preferably, "aryl" refers to phenyl, tolyl and methoxyphenyl.

Detailed Description Text (21):
R.sup.11, R.sup.12 and R.sup.13 are each independently selected from the group consisting of H, halogen, C.sub.1 -C.sub.20 alkyl (preferably C.sub.1 -C.sub.10 alkyl and more preferably C.sub.1 -C.sub.6 alkyl), C.sub.3 -C.sub.8 cycloalkyl, C(.dbd.Y)R.sup.5, C(.dbd.Y)NR.sup.6 R.sup.7 (where R.sup.5 -R.sup.7 are as defined above), COCl, OH (preferably only one of R.sup.11, R.sup.12 and R.sup.13 is OH) , CN, C.sub.2 -C.sub.20 alkenyl or alkynyl (preferably C.sub.2 -C.sub.6 alkenyl or alkynyl, and more preferably vinyl), oxiranyl, glycidyl, aryl, heterocyclyl, aralkyl, aralkenyl (aryl-substituted alkenyl, where aryl is as defined above, and alkenyl is vinyl which may be substituted with one or two C.sub.1 -C.sub.6 alkyl groups and/or halogen atoms [preferably chlorine]), C.sub.1 -C.sub.6 alkyl in which from 1 to all of the hydrogen atoms (preferably 1) are replaced with halogen (preferably fluorine or chlorine where 1 or more hydrogen atoms are replaced, and preferably fluorine, chlorine or bromine where 1 hydrogen atom is replaced) and C.sub.1 -C.sub.6 alkyl substituted with from 1 to 3 substituents preferably 1) selected from the group consisting of C.sub.1 -C.sub.4 alkoxy, aryl, heterocyclyl, C(.dbd.Y)R.sup.5 where R.sup.5 is as defined above) C(.dbd.Y)NR.sup.6 R.sup.7 (where R.sup.6 and R.sup.7 are as defined above), oxiranyl and glycidyl; such that no more than two of R.sup.11, R.sup.12 and R.sup.13 are H (preferably no more than one of R.sub.11, R.sup.12 and R.sup.13 is H).

Detailed Description Text (23):
When an alkyl, cycloalkyl, or alkyl-substituted aryl group is selected for one of R.sup.11, R.sup.12, and R.sup.13, the alkyl group may be further substituted with an X group as defined above. Thus, it is possible for the initiator to serve as a starting molecule for branch or star (co)polymers. One example of such an initiator is a 2,2-bis(halomethyl)-1,3-dihalopropane (e.g., 2,2-bis(chloromethyl)-1,3-dichloropropane, 2,2-bis(bromomethyl)-1,3-dibromopropane), and a preferred example is where one of R.sup.11, R.sup.12 and R.sup.13 is phenyl substituted with from one to five C.sub.1 -C.sup.6 alkyl substituents, each of which may independently be further substituted with a X group (e.g., .alpha.,.alpha.'-dibromoxylene, hexakis(.alpha.-chloro- or .alpha.-bromomethyl)benzene).

Detailed Description Text (34):
each R.sup.18 is independently a divalent group selected from the group consisting of C.sub.2 -C.sub.4 alkylene (alkanediyl) and C.sub.2 -C.sub.4 alkenylene where the covalent bonds to each Z are at vicinal positions (e.g., in a 1,2-arrangement) or at .beta.-positions e,g., in a 1,3-arrangement), and from C.sub.3 -C.sub.8 cycloalkanediyl, C.sub.3 -C.sub.8 cycloalkenediyl, arenediyl and heterocyclylene where the covalent bonds to each Z are at vicinal positions; and

Detailed Description Text (39):
Further ligands suitable for use in the present invention include compounds of the formula R.sup.20 R.sup.21 C(C(.dbd.Y)R.sup.5).sup.2, where Y and R.sup.5 are as defined above, and each of R.sup.20 and R.sup.21 is independently selected from the group consisting of H. halogen, C.sub.1 -C.sub.20 alkyl, aryl and heterocyclyl, and R.sup.20 and R.sup.21 may be joined to form a C.sub.3 -C.sub.8 cycloalkyl ring or a hydrogenated (i.e., reduced, non-aromatic or partially or fully saturated) aromatic or heterocyclic ring (consistent with the definitions of "aryl" and "heterocyclyl" above), any of which (except for H and halogen) may be further substituted with 1 to 5 and preferably 1 to 3 C.sub.1 -C.sub.6 alkyl groups, C.sub.1 -C.sub.6 alkoxy groups, halogen atoms and/or aryl groups. Preferably, one of R.sup.20 and R.sup.21 is H or a negative charge.

Detailed Description Text (46):
The present polymerization may be conducted in the absence of solvent ("bulk" polymerization). However, when a solvent is used, suitable solvents include ethers, cyclic ethers, C.sub.5 -C.sub.10 alkanes, C.sub.5 -C.sub.8 cycloalkanes which may be substituted with from 1 to 3 C.sub.1 -C.sub.4 alkyl groups, aromatic hydrocarbon solvents, halogenated hydrocarbon solvents, acetonitrile, dimethylformamide, mixtures of such solvents, and supercritical solvents (such as CO.sub.2, C.sub.1

-C.sub.4 alkanes in which any H may be replaced with F, etc.). The present polymerization may also be conducted in accordance with known suspension, emulsion and precipitation polymerization processes.

Detailed Description Text (54):
Precipitation can be typically conducted using a suitable C.sub.5 -C.sub.8 -alkane or C.sub.5 -C.sub.8 -cycloalkane solvent, such as pentane hexane, heptane, cyclohexane or mineral spirits, or using a C.sub.1 -C.sub.6 -alcohol, such as methanol, ethanol or isopropanol, or any mixture of suitable solvents. Preferably, the solvent for precipitating is hexane, mixtures of hexanes, or methanol.

Detailed Description Text (70):
Preferably, at least one of M.sup.1 and M.sup.2 has the formula: ##STR6## wherein at least one of R.sup.1 and R.sup.2 is CN, CF.sub.3, straight or branched alkyl of from 4 to 20 carbon atoms (preferably from 4 to 10 carbon atoms, more preferably from 4 to 8 carbon atoms), C.sub.3 -C.sub.8 cycloalkyl, aryl, heterocyclyl, C(.dbd.Y)R.sup.5, C(.dbd.Y)NR.sup.6 R.sup.7 and YC(.dbd.Y)R.sup.8, where aryl, heterocyclyl, Y, R.sup.5, R.sup.6, R.sup.7 and R.sup.8 are as defined above; and

CLAIMS:

5. The process of claim 1, wherein said monomer(s) are of the formula: ##STR11## wherein R.sup.1 and R.sup.2 are independently selected from the group consisting of H, halogen, CN, CF.sub.3, straight or branched alkyl of from 1 to 20 carbon atoms, .alpha.,.beta.-unsaturated straight or branched alkenyl or alkynyl of 2 to 10 carbon atoms, .alpha.,.beta.-unsaturated straight or branched alkenyl of 2 to 6 carbon atoms substituted with halogen, C.sub.3 -C.sub.8 cycloalkyl, phenyl which may optionally have from 1 to 5 substituents on the phenyl ring selected from the group consisting of C.sub.1 -C.sub.6 -alkyl, C.sub.1 -.sub.6 -alkenyl, C.sub.1 -C.sub.6 -alkoxy, halogen, nitro, carboxy, C.sub.1 -C.sub.6 -alkoxycarbonyl, hydroxy protected with a C.sub.1 -C.sub.6 -acyl, cyano and phenyl, heterocyclyl, C(.dbd.Y)R.sup.5, C(.dbd.Y)NR.sup.6 R.sup.7, YCR.sup.6 R.sup.7 R.sup.8 and YC(.dbd.Y)R.sup.8 ; where Y may be NR.sup.8 or O; R.sup.5 is alkyl of from 1 to 20 carbon atoms, alkoxy of from 1 to 20 carbon atoms, aryloxy or heterocyclyloxy; R.sup.6 and R.sup.7 are independently H or alkyl of from 1 to 20 carbon atoms, or R.sup.6 and R.sup.7 may be joined together to form an alkylene group of from 2 to 5 carbon atoms, thus forming a 3- to 6-membered ring; and R.sup.8 is H, straight or branched C.sub.1 -C.sub.20 alkyl or aryl; and

R.sup.3 and R.sup.4 are independently selected from the group consisting of H, halogen, C.sub.1 -C.sub.6 alkyl and COOR.sup.9, where R.sup.9 is H, an alkali metal, or a C.sub.1 -C.sub.6 alkyl group; or

R.sup.1 and R.sup.3 may be joined to form a group of the formula (CH.sub.2).sub.n' or a group of the formula C(.dbd.O)--Y--C(.dbd.O), where n' is from 2 to 6, the group (CH.sub.2).sub.n' may be substituted with from 1 to 2n' halogen atoms or C.sub.1 -C.sub.4 alkyl groups, and Y is as defined above; and

at least two of R.sup.1, R.sup.2, R.sup.3 and R.sup.4 are H or halogen.

6. The process of claim 1, wherein said initiator is of the formula:

R.sup.11 R.sup.12 R.sup.13 C--X

where:

X is selected from the group consisting of Cl, Br, I, OR.sup.10, SR.sup.14, SeR.sup.14, OP(.dbd.O)R.sup.14, OP(.dbd.O) (OR.sup.14).sub.2, OP(.dbd.O)OR.sup.14, O--N(R.sup.14).sub.2 and S--(.dbd.S)N(R.sup.14).sub.2, where R.sub.10 is alkyl of from 1 to 20 carbon atoms in which each of the hydrogen atoms may be independently replaced by halide, R.sup.14 is aryl or a straight or branched C.sub.1 -C.sub.20 alkyl group, and where an N(R.sup.14).sub.2 group is present, the two R.sup.14 groups may be joined to form a 5- or 6-membered heterocyclic ring; and

R.sup.11, R.sup.12, and R.sup.13 are each independently selected from the group

consisting of H, halogen, C.sub.1 -C.sub.20 alkyl, C.sub.3 -C.sub.8 cycloalkyl, X(.dbd.Y)R.sup.5, C(.dbd.Y)NR.sup.6 R.sup.7, COCl, OH, CN, C.sub.2 -C.sub.20 alkenyl, C.sub.2 -C.sub.20 alkynyl oxiranyl, glycidyl, aryl, heterocyclyl, aralkyl, aralkenyl, C.sub.1 -C.sub.6 alkyl in which from 1 to all of the hydrogen atoms are replaced with halogen and C.sub.1 -C.sup.6 alkyl substituted with from 1 to 3 substituents selected from the group consisting of C.sub.1 -C.sub.4 alkoxy, aryl, heterocyclyl, C(.dbd.Y) R, C(.dbd.Y)NR.sup.6 R.sup.7, oxiranyl and glycidyl;

where R.sup.5 is alkyl of from 1 to 20 carbon atoms, alkoxy of from 1 to 20 carbon atoms, aryloxy or heterocyclyloxy; and R.sup. 6 and R.sup.7 are independently H or alkyl of from 1 to 20 carbon atoms, or R.sup.6 and R.sup.7 may be joined together to form an alkylene group of from 2 to 5 carbon atoms, thus forming a 3- to 6-membered ring; such that no more than two of R.sup.11, R.sup.12 and R.sup.13 are H.

9. The process of claim 1, wherein said ligand is selected from the group consisting of:

compounds of the formulas:

R.sup.16 --Z--Z.sup.17

R.sup.16 --Z--(R.sup.18 --Z).sub.m --R.sup.17

where:

R.sup.16 and R.sup.17 are independently selected from the group consisting of H, C.sub.1 -C.sub.20 alkyl, aryl, heterocyclyl and C.sub.1 -C.sub.6 alkyl substituted with C.sub.1 -C.sub.6 alkoxy, C.sub.1 -C.sub.4 dialkylamino, C(.dbd.Y R.sup.5, C(.dbd.Y)R.sup.6 R.sup.7 and YC(.dbd.Y)R.sup.8, where Y may be NR.sup.8 or O; R.sup.5 is alkyl of from 1 to 20 carbon atoms, alkoxy of from 1 to 20 carbon atoms, aryloxy or heterocyclyloxy; R.sup.6 and R.sup.7 are independently H or alkyl of from 1 to 20 carbon atoms, or R.sup.6 and R.sup.7 may be joined together to form an alkylene group of from 2 to 5 carbon atoms, thus forming a 3- to 5-membered ring; and R.sup.8 is H, straight or branched C.sub.1 -C.sub.20 alkyl or aryl;

Z is O, S, NR.sup.19 or PR.sup.19, where R.sup.19 is selected from the same group as R.sup.16 and R .sup.7, and where Z is PR.sup.19, R.sup.19 can also be C.sub.1 -C.sub.20 -alkoxy;

each R.sub.18 is independently a divalent group selected from the group consisting of C.sub.3 -C.sub.3 cycloalkanediyl, C.sub.3 -C.sub.8 cycloalkenediyl, arenediyl and heterocyclylene where the covalent bonds to each Z are at vicinal positions, and C.sub.2 -C.sub.4 alkylene and C.sub.2 -C.sub.4 alkenylene where the covalent bonds to each Z are at vicinal positions or at .beta.-positions; and

m is from 1 to 6;

compounds of the above formulas where R.sup.16 and R.sup.17 can be joined to form a saturated, unsaturated or heterocyclic ring;

compounds of the above formulas where each of R.sup.16 --Z and R.sup.17, form a ring with the R.sup.18 group to which the Z is bound to form a linked or fused heterocyclic ring system;

compounds of the above formulas where one or both of R.sup.16 and R.sup.17 are heterocyclyl, and in which Z is a covalent bond, CH.sub.2 or a 4- to 7-membered ring fused to R.sup.15 or R.sup.17 or both;

CO;

porphyrins and porphycenes, which may be substituted with from 1 to 6 halogen atoms, C.sub.1 -C.sub.6 alkyl groups, C.sub.1 -C.sub.6 -alkoxy groups, C.sub.1 -C.sub.6 alkoxycarbonyl, aryl groups, heterocyclyl groups, and C.sub.1 -C.sub.6 alkyl groups further substituted with from 1 to 3 halogens;

compounds of the formula R.sup.20 R.sup.21 C(C(.dbd.Y)R.sup.5).sub.2 where Y and R.sup.5 are as defined above, and each of R.sup.20 and R.sup.21 is independently selected from the group consisting of H, halogen, C.sub.1 -C.sub.20 alkyl, aryl and heterocyclyl, and R.sup.20 and R.sup.21 may be joined to form a C.sub.3 -C.sub.8 cycloalkyl ring or a hydrogenated aromatic or heterocyclic ring, any of which (except for H and halogen) may be further substituted with 1 to 5 C.sub.1 -C.sub.6 alkyl groups, C.sub.1 -C.sub.6 alkoxy groups, halogen atoms, aryl groups, or combinations thereof; and

arenes and cyclopentadienyl ligands, where said cyclopentadienyl ligand may be substituted with from one to five methyl groups, or may be linked through an ethylene or propylene chain to a second cyclopentadienyl ligand.

reagent (C), of formula (V) , which breaks the chain after the monomer is used up, and contains a functional group Y, as defined above, and an R17 group between the double bond and Y; R<14>,R<15>,R<16> = H, aryl, or halo substituted alkyl, prepared by living radical polymerization; and R<17> = linear or branched, optionally substituted alkyl chain of at least one -CH2- group.